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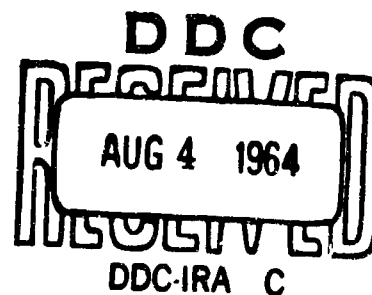
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Title: VAPOR-PHASE REACTIONS OF ORGANIC COMPOUNDS WITH OXYGEN

Prepared by

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Prepared for

U.S. Army Chemical Research and Development Laboratories
Edgewood Arsenal, Maryland

SUMMARY

The Summary appears both on the abstract cards and as Section 3 of this report.

INDEX

TABLES

1.   OBJECTIVES

The short-term objective of this work is to obtain information on the kinetics and mechanisms of gas-phase oxidations of simple and substituted alkanes and alkenes and on possible means of accelerating such oxidations. The long-term objective is to obtain information on oxidations of substituted hydrocarbons for possible applications in decontamination.

2.   PREVIOUS WORK

Although hydroperoxides are the principal primary products of most homogeneous liquid-phase oxidations up to about 160°, they have seldom been reported in more than small quantities in gas-phase oxidations. In previous, privately supported work, we set out to determine whether hydroperoxides could be obtained in good yields in gas-phase oxidations under the most favorable conditions.

The initiated oxidation of isobutane at 155° at about 200-500 mm gave acetone and methanol as major products and only small amounts of t-butyl alcohol and t-butyl hydroperoxide. We interpreted these results to mean that most t-butylperoxy radicals interacted with each other to give t-butoxy radicals and oxygen. A few t-butoxy radicals attacked isobutane but most cleaved to acetone and methyl radicals which, by the process above, were converted to methoxy radicals. The high yields of methanol indicated that most of the attack on isobutane was by methoxy radicals. The low yields of hydroperoxide are thought to come from a termination reaction involving t-butylperoxy and methoxy radicals.

The di-t-butyl peroxide-initiated oxidation of cyclopentene at 155°, below a total pressure of one atmosphere, proceeded a little faster. The products, mostly cyclopentenol, cyclopentenone, and cyclopentene oxide, might be decomposition products of hydroperoxides.

3.   SUMMARY

A series of gas-phase, peroxide-initiated oxidations of isobutane was carried out at 100° with pressures of isobutane ranging from 1 to 13 atmospheres. The yields of hydroperoxide increased with increasing pressure: from 16% at one atmosphere to 92% at 13 atmospheres (with < 1% conversion of isobutane). A large increase in surface area did not affect the rate of oxidation or the yield of hydroperoxide. The increased yields of hydroperoxide at higher concentrations of hydrocarbon are due partly to an increased rate of chain propagation and partly to protection of the hydroperoxide (by the hydrocarbon) from induced decomposition. The rate of the $t-Bu_2O_2$-induced decomposition of t-butyl hydroperoxide in the gas phase at 100° in the absence of oxygen depends on the kind and concentration of added hydrocarbon.

Liquid-phase data on the oxidations of isobutane at 50° and 80° have been used to estimate rates of oxidation, kinetic chain lengths, and times

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for 99% conversion for oxidations of liquid isobutane and very dilute gaseous isobutane at 30°. Rates are much too low for decontamination purposes and some expedients are suggested.

The gas-phase oxidation of cyclopentene at 1-3 atmospheres at 100° and 155° gave hydroperoxide (and its decomposition products), epoxide and unidentified high-boiling materials in proportions which depend on the concentration of cyclopentene. The liquid-phase oxidation at 100° (and below) gave more than 90% yield of hydroperoxide. The vapor-phase decomposition of cyclopentenyl hydroperoxide was not accelerated by t Bu$_2$O$_2$, or retarded by cyclopentene, but was retarded by benzene; it appears to be a non-radical reaction.

Two postulates have been applied to literature data on the gas-phase oxidation of isobutylene and found to provide a useful correlation. Hydrogen bromide catalysis of this oxidation is discussed briefly.

Catalysis by hydrogen chloride of free radical chain oxidations of hydrocarbons by alkoxy radical carriers is proposed and discussed. Experimental evidence of this catalysis is presented but clear proof is lacking.

4. GAS-PHASE OXIDATION OF ISOBUTANE; STABILIZATION OF t-BUTYL HYDROPEROXIDE

4.1. Rate and Phase Effects

Since a low concentration of hydrocarbon seemed to be responsible for low rates of oxidation of isobutane, a series of peroxide-initiated gas-phase oxidations of isobutane was carried out at 100° at isobutane pressures of 1 to 13 atmospheres. Both oxygen concentration (~ 0.01 M) and rate of initiation by di-t-butyl peroxide were held nearly constant. Table I summarizes the rate and product data. The average rates of oxidation over this range fit the simple rate law based on bimolecular termination by 2RO$_2$·,

$$R_{O_2} = (R_i/2k_t)^{1/2} \, k_p[RH]$$

where $R_i = 2k_i[R_2O_2]$. With the omission of Expts. 17D, 31E, and 32B (which contained added materials), values of $k_p/k_t^{1/2}$ average 0.0090 and all lie within 14% of this value; Expt. 31B at 90° gave a lower but consistent value of $k_p/k_t^{1/2}$.

Extrapolation of our value for the liquid-phase oxidation of isobutane at 80° to 100° gives a value of 0.00525 liter/mol$^{1/2}$min$^{1/2}$ for $k_p/k_t^{1/2}$ compared to our gas-phase value of 0.0090. This 70% increase in rate in going from the liquid phase to gas phase is based on one measured value at 80° and is comparable to effects of solvent polarity found in the oxidations of styrene[1] and cyclohexane.[2] The change in rate with isobutane probably is not due to a change in termination mechanism from

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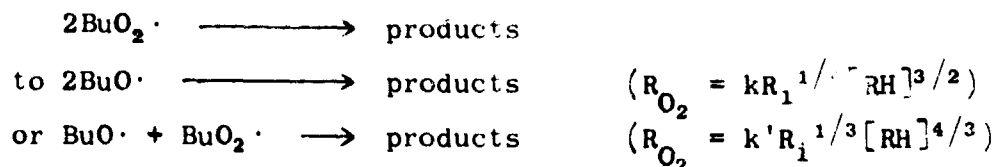[1] J. A. Howard and K. U. Ingold, Can. J. Chem., **42**, 1044 (1964).
[2] D. G. Hendry and G. A. Russell, paper to appear in J. Am. Chem. Soc.

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Table I

OXIDATION OF ISOBUTANE AT 100°[a]

	32A	31C	17D	17C	31D	31E	32B[d]	17F	31B[a]
Run Number									
Time (min)	6025	1666	990	990	906	908	900	982	1,586
Reaction Volume (ml)	143	104	102	102	105	77	139[d]	102	105
Reactants									
i-BuH Pressure (atmospheres)	1.05	3.21	7.32	6.54	6.27	8.34	6.65	13.2	12.23
iBuH, mols/liter	0.0337	0.102	0.233	0.208	0.202	0.269	0.214	0.420	0.394
iBuH	4,820	10,750	23,800	21,200	21,220	20,710	29,800	43,600	41,410
t-Bu$_2$O$_2$ } micromols	126	98	98	110	102	98	143	100	102
O$_2$ } micromols	1,408	1,015	1,009	991	1,817	1,099	1,379	1,022	1,072
Other			50.7 ROOH			52 HCl			
Products, micromols									
-O$_2$	65	33	43	43	46	56	62	96	62
t-Bu$_2$O$_2$ calculated[b]	20.6	4.9	2.9	3.3	2.8	2.7	3.9	2.9	1.2
CO	7	0	1	0	0	0	15	5	1.5
Acetone	32	17	-	17	-	-	-	-	9
MeOH	<5	<4	-	<2	-	-	-	-	<5
t-BuOH	13	15-18	-	20	-	-	-	-	11
ROOH[c]	10.4	15	82 (31)	21	27	33	35	88	51
% O$_2$ as ROOH	16	45	71	49	59	59	56	92	82
R$_{O_2}$ mols/liter min x 10^8	7.5	19	41.3	41.3	48.4	80	50	95	37.3
R$_1$ mols/liter min x 10^8[b]	4.8	5.6	5.8	6.5	5.9	7.0	6.2	5.8	1.5
R$_{O_2}$/R$_1$ (chain length)	1.6	3.4	7.1	6.3	8.2	11	8.0	16	25
R$_{O_2}$/R$_1^{\frac{1}{2}}$[iBuH] = k$_p$k$_t^{\frac{1}{2}}$; x 10^3	10.2	7.9	7.4	7.8	9.9	11	9.4	9.4	7.8

[a] 31B at 90°.

[b] k_d at 100° = 5.0 x 10^{-7}/sec. (Ref. 3). R_1 = 2k_d.

[c] By iodometric titration.

[d] 3.69 g glass wool added. Surface:volume ratio increased 100-1000 fold.

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$$2BuO_2 \cdot \longrightarrow \text{products}$$

$$\text{to } 2BuO \cdot \longrightarrow \text{products} \qquad (R_{O_2} = kR_i^{1/2}[RH]^{3/2})$$

$$\text{or } BuO \cdot + BuO_2 \cdot \longrightarrow \text{products} \qquad (R_{O_2} = k'R_i^{1/3}[RH]^{4/3})$$

because our rate data do not fit either of the indicated rate laws.

4.2. Hydroperoxide Formation in Gas-Phase Oxidations

At 13 atmospheres of isobutane (Run 17F), over 90% of the consumed oxygen appears as hydroperoxide. Gas chromatography shows that the hydroperoxide is mostly t-butyl hydroperoxide and the chain length is long enough (16) to exclude more than a 7% contribution to hydroperoxide formation by the termination reaction:

$$BuO_2 \cdot + CH_3O \cdot \longrightarrow BuOOH + CH_2O$$

The low yields of methanol and CO compared to the yields of acetone (1 acetone = 1 Me·) in some experiments suggest that MeO_2H could be present. The yield of hydroperoxide at high isobutane pressures parallels the results from our liquid-phase reactions at 50° and 80°, and also at 125°[4] where high yields of hydroperoxide were realized. Although yields of hydroperoxide decrease with decreasing isobutane concentration, there is some variation in yields of hydroperoxide at similar pressures (17C, 17D, 31D, 31E, 32B).

There are at least two factors responsible for the low yields of hydroperoxides generally found in gas-phase oxidations: (1) The propagation chain carrier changes from peroxy radical to alkoxy radical which is better able to abstract at low temperatures. (2) The hydroperoxides formed are subject to induced decomposition by alkoxy radicals at low hydrocarbon concentrations.

If we consider a simple oxidation scheme in which autocatalysis is unimportant, the following reactions govern hydroperoxide formation:

$$ROOR \xrightarrow{k_1} 2RO \cdot \qquad (1)$$

$$RO \cdot + RO_2H \longrightarrow ROH + RO_2 \cdot \qquad (2)$$

$$RO \cdot + RH \longrightarrow ROH + R \cdot \qquad (3)$$

$$R \cdot + O_2 \longrightarrow RO_2 \cdot \qquad (4)$$

$$RO_2 \cdot + RH \xrightarrow{k_p} RO_2H + R \cdot \qquad (5)$$

$$2RO_2 \cdot \longrightarrow 2RO \cdot + O_2 \qquad (6)$$

$$2RO_2 \xrightarrow{k_t} \text{termination} \qquad (7)$$

[3] L. Batt and S. W. Benson, J. Chem. Phys., **36**, 895 (1962).
[4] D. E. Winkler and G. W. Hearne, Ind. Eng. Chem., **53**, 655 (1961).

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Application of steady-state conditions for each radical gives

$$\frac{d[ROOH]}{dt} = R_{O_2} - \frac{R_i k_2 [ROOH](1 + k_6/k_t)}{k_2[ROOH] + k_3[RH]} \qquad (8)$$

$$\text{where } R_{O_2} = (\frac{R_i}{k_t})^{1/2} k_p[RH]$$

These relations show that the rate of peroxide formation (reaction 5, R_{O_2}) is offset by reaction 2 and assisted by reaction 3 (which helps to re-place the peroxide decomposed). These two reactions should have similar rate constants since the bond dissociation energies of t-Bu-H and t-BuO$_2$-H are nearly equal. Hence, when the concentration of hydrocarbon is high compared with hydroperoxide, little of the latter will be decomposed, but as the concentration of hydrocarbon decreases, equation 8 approaches an expression for the induced decomposition (without formation) of hydroper-oxide. Thus, net production of hydroperoxide is favored by an excess of hydrocarbon over hydroperoxide in either liquid-phase or vapor-phase. Further, since k_2 depends little on the structure of R· while both k_3 and k_p decrease as R· changes from tertiary to primary, equation 8 indicates that the hydroperoxides which are hardest to make will also be hardest to protect. These relations assume that the uninduced decomposition of hydroperoxide is negligible. Experiment 17D shows that such is the case in the experiments in Table I.

4.3. Effect of Added Materials

Several materials were added to isobutane oxidation mixtures:

(1) Addition of Pyrex glass wool to run 32B increased the surface area by a factor of 100-1000 (assuming a tenfold variation in diameter of individual strands). No effect was noted either on the rate of oxida-tion or on the yield of hydroperoxide, compared with similar runs with no added surface. This result demonstrates the purely homogeneous nature of these oxidations at 100°.

(2) The comparative insensitivity of rate to added t-butyl hydro-peroxide in Run 17D was noted above: our assumption that autocatalysis is absent at low conversions ($< 1\%$) and temperatures is confirmed. The somewhat higher yield of hydroperoxide found in 17D compared to 17C or 31D is probably within experimental error.

(3) Evidence for catalysis by HCl during oxidation was sought by adding 50 micromoles of HCl to Run 31E. HCl catalysis is expected with alkoxy radical chain carriers (Section 7). The value of $k_p/k_t^{1/2}$ indicates a 15-20% increase in rate -- not great but perhaps significant when it is considered that 59% of the oxygen is consumed in a peroxy radical chain.

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4.4. Gas-Phase Decomposition of t-Butyl Hydroperoxide in Near-Absence of Oxygen

Reactions 1-7 and equation 8 show how hydrocarbons can stabilize hydroperoxides in oxidizing systems; by diverting alkoxy radicals from reaction 2 by means of reaction 3, they not only protect hydroperoxides but they produce new hydroperoxide through reactions 4 and 5. In this section, we are concerned primarily with marked stabilization of peroxides by some hydrocarbons in the near-absence of oxygen (some must be formed in the decomposition) and in the presence of radical sources. Now reaction 3 will offer no protection if the R· produced there only regenerates RO_2· by the reverse of reaction 5; for protection in the absence of oxygen the R·'s must participate in chain termination with each other or with RO· or RO_2·. The major factor in protection is still the ability of reaction 3 to compete with chain termination. Thus the rate of decomposition of peroxide will be a complex function of peroxide:hydrocarbon ratio. Liquid-phase studies have shown such relations and these have commonly been attributed to complex formation.[3] Complex formation should be absent at low concentrations in the gas phase and such studies may provide a useful insight on the nature of the decomposition of hydroperoxides in hydrocarbon solvents.

Mixtures of constant amounts of t-butyl hydroperoxide and di-t-butyl peroxide (2:1) were heated in air-free, 100 ml sealed glass bulbs at 100° for various intervals with various amounts of added hydrocarbons. Hydroperoxide contents were then determined iodometrically after careful low-temperature distillation of hydrocarbon. Rates of decomposition measured in these hydrocarbons will be somewhat high if some peroxide distills with the hydrocarbon. In formaldehyde experiments, a modified procedure[6] was used to ensure complete reduction of the hydroperoxide-formaldehyde addition product.

Table II summarizes our results with t-butyl hydroperoxide with and without initiator and hydrocarbons. Experiments without hydrocarbon and without di-t-butyl peroxide initiator (40A, 40D) show that the self-initiated reaction is only 10% as fast as the $t-Bu_2O_2$-initiated reaction where a chain length of 14 is indicated. Addition of isobutane slows the rate of decomposition; a sixfold increase in the isobutane pressure decreases the rate of destruction of hydroperoxide by 95%. (At ~ 5% conversions of hydroperoxide the rates could be in error by a factor of three.) However, 6 atmospheres of n-butane shows little retarding effect (Run 40C), but even one-seventh of this amount of cyclopentene greatly retards destruction of hydroperoxide (Run 40E). The general order of effectiveness of the hydrocarbons as retarders of the hydroperoxide decomposition is that expected from their abilities to donate hydrogen atoms in reaction 3: cyclopentene > isobutylene > cyclopentane > n-butane.

Formaldehyde is a surprisingly effective catalyst for the hydroperoxide decomposition (43 L, I, K); the retarding effect of added cyclopentene

[3]L. Bateman and H. Hughes, J. Chem. Soc., 1952, 4549
[6]R. Hiatt and W. M. J. Strachan, J. Org. Chem., 28, 1894 (1963).

Table II

EFFECTS OF ADDED MATERIALS ON GAS-PHASE DECOMPOSITIONS OF HYDROPEROXIDES AT 100°

Expt.	Time (min)	Reactants, mols/liter x 10^3					Rates, mols/liter min x 10^7	
		RH		$t-BuO_2H$ Initial	$t-BuO_2H$ Final	$t-Bu_2O_2$	$-[RO_2H]dt$	R_i Calc.[b]
40A	360		0	2.44	2.40	0	1.1	--
40D	360		0	2.00	1.63	0.95	10.3	0.57
39A	360	i-BuH	45.3	2.28	1.43	1.15	10.6	0.69
39B	675	i-BuH	129.7	2.32	1.95	1.19	4.6	0.71
39C	900	i-BuH	273[a]	2.20	2.14	1.05	0.55	0.63
17E	985	i-BuH	215	0.503	0.473	0.95	0.31	0.57
39D	900	i-BuH	237[c]	2.26	1.54[d]	1.14	6.7[d]	0.68
39E	Blank 0	i-BuH	239[c]	2.13	2.02	0		
40C	360	n-BuH	214	2.00	1.71	1.06	8.06	0.64
43A	360	n-BuH	369	1.87	1.73	1.01	3.9	0.61
43C	900	n-BuH	359	1.97	1.87	1.01	1.1	0.61
40E	480	C_5H_8	29.4	2.04	2.00	0.97	0.83	0.58
40B	360	C_5H_8	66.7	1.99	1.98	1.00	0.28	0.60
43H	900	C_5H_{10}	249	1.82	1.74	0.92	0.90	0.55
43F	900	$i-C_4H_8$	222	2.04	1.95	1.05	1.0	0.63
43G	900	$i-C_4H_8$	405	2.04	1.97	1.04	0.72	0.62
43L	30	CH_2O	5.31	1.97	1.64[e]	0.99	110	0.59
43I	240	CH_2O	6.00	2.07	0.96[e]	0.94	46	0.56
43K	360	C_5H_8 60 CH_2O 6.0		1.98	1.12[e]	1.10	24	0.66

[a] The total pressure in Run 39C was about 7 atmospheres; other pressures can be estimated from this datum.
[b] From $t-Bu_2O_2$, note b in Table I.
[c] Glass wool added, sufficient to increase surface:volume ratio by about 100.
[d] Corrected for adsorption loss of ROOH on glass-wool as indicated from Run 39F where only 2.02 out of 2.13 micromols/liter were recovered with no heating.
[e] Titrated after heating with KI in HOAc-PrOH at 70° for 20 minutes.[5]

may be due to the longer time of the experiment. Since many gas-phase oxidations produce formaldehyde via methoxy or methyl radicals cleaved from larger radicals, this aldehyde may also contribute to the low yields of hydroperoxides commonly obtained in gas-phase oxidations.

Run 39E was carried out with an almost 100-fold increase in surface to volume ratio by addition of glass wool. The rate of peroxide decomposition increased 14-fold compared to Run 39C. This increase probably reflects a surface-catalyzed decomposition of hydroperoxide in the absence of oxygen.

4.5. Rates of Oxidation of Isobutane at 30°

Since rate constants for oxidation of isobutane are similar in both the liquid and gas phases (Section 4.1) and since isobutane is neither unusually reactive nor unreactive, some calculations are given below for their implications for problems relating to decontamination. From unpublished liquid-phase data of D. G. Hendry at 50° and 80°, the following relation is available for 30°C: ($Ea = 9.5$ kcal)

$$k_p/(2k_t)^{1/2} = 0.010 \text{ (liter hour/mol)}^{1/2}$$

Calculations in Tables III and IV are also based on the relations:

$$\frac{-d[RH]}{dt} = \left(\frac{R_i}{2k_t}\right)^{1/2} k_p[RH]$$

$$\text{Chain length} = \frac{-d[RH]/dt}{R_i} = \frac{k_p[RH]}{(2R_ik_t)^{1/2}}$$

The time for 99% conversion of RH at constant R_i =

$$t = 4.6(2k_t/R_i)^{1/2}/k_p$$

These relations assume that $k_p/k_t^{1/2}$ for the initiating radical is the same as for $t\text{-BuO}_2\cdot$ radicals.

For neat liquid (10 M) hydrocarbon, Table III indicates chain lengths (mols of RH consumed per initiating radical), rates of reaction of hydrocarbon, and times for 99% conversion (from an integrated equation for a system without complications) in a simple homogeneous oxidation at 30°. Times for 90% conversion will be one-half those for 99%; for 50%, about one-seventh of those for 99%. This table shows, for example, that if one wants a chain length of 100, radicals must be supplied so slowly that 500,000 hours would be required for 99% conversion. At the other extreme, if initiating radicals are supplied at the rate of 10,000 mols/liter/hour, 99.9% of them will be wasted initially, and 99.999% of them will be wasted at 99% conversion, which will require 5 hours.

On the other hand, if the hydrocarbon is present as a vapor in air at 25 ppm, its concentration is 10^{-6} M. Table IV gives estimates and chain lengths under these conditions. Because of the very low concentration of hydrocarbons, rates and chain lengths are much lower for the same rate of initiation. For 10 times as much hydrocarbon, the chain lengths and rates in mols/liter/hour would be 10 times as great, and so on. However, for the same rates of initiation, the rates in %/hour and the times for 99% conversion are independent of concentration and are the same in the two tables.

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Table III

ESTIMATED RATES OF OXIDATION OF LIQUID ISOBUTANE AT 30°

R_i $\frac{mol}{liter\ hour}$	Chain Length	Initial $-d[RH]/dt$		t for 99% Conv. (hr)
		(mole/liter/hr)	(% per hr)	
10^{-6}	100	0.0001	0.001	500,000
10^{-4}	10	0.001	0.01	50,000
10^{-2}	1	0.01	0.1	5,000
1	0.1	0.1	1	500
10^2	0.01	1.0	10	50
10^4	0.001	10	100	5

Table IV

ESTIMATED RATES OF OXIDATION OF 25 ppm OF ISOBUTANE VAPOR IN AIR AT 30°

R_i $\frac{mol}{liter\ hour}$	Chain Length	$-d[RH]/at$		t for 99% Conversion hr
		$\frac{mol}{liter\ hour}$	%/hr	
10^{-20}	100	10^{-18}	10^{-10}	5×10^{12}
10^{-18}	10	10^{-17}	10^{-9}	5×10^{11}
10^{-16}	1	10^{-16}	10^{-8}	5×10^{10}
10^{-12}	0.01	10^{-14}	10^{-6}	5×10^{8}
10^{-8}	10^{-4}	10^{-12}	10^{-4}	5×10^{6}
10^{-4}	10^{-6}	10^{-10}	0.01	5×10^{4}
1	10^{-8}	10^{-8}	1	500

These calculations show that conventional homogeneous oxidations are probably hopelessly slow for decontamination purposes at 30°. Rates of oxidation might be increased above those estimated in the following ways: (1) by making more use of alkoxy radicals as chain carriers (reactions 3, 4, and 6), (2) by use of hydrogen chloride or other catalytic transfer agents in reaction chains (Section 7), (3) by employing higher temperatures, (4) 'y utilizing heterogeneous reactions, (5) by utilizing a more favorable $k_p/k_t^{1/2}$ ratio by (5a) restricting chain termination by use of aerosol, emulsion, or similar techniques, or by (5b) utilizing a more reactive radical than $RO_2 \cdot$ for chain initiation (as $F \cdot$ or $Cl \cdot$), or (6) by burning a larger (but still small) amount of cheap and innocuous hydrocarbon (a combination of more radicals and higher temperatures).

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5. GAS-PHASE OXIDATION OF CYCLOPENTENE; DECOMPOSITION OF CYCLOPENTENYL HYDROPEROXIDE

Because cyclopentene reacts readily to give high yields of hydroperoxide (93% at 50°) in the liquid-phase oxidation, its gas-phase oxidation was of interest.

5.1. Oxidation of Cyclopentene at 155°

Table V summarizes results of a series of oxidations with cyclopentene, oxygen, and di-t-butyl peroxide in which the pressure of cyclopentene was changed 16-fold up to almost the saturation vapor pressure at both 155° and 100°. The runs at 155° show that on increasing the cyclopentene pressure from 183 mm to 1140 mm (with one-third the initiator and five times the oxygen) the rate remains about the same although the average chain length has increased proportionately. Assuming one O_2 per initiator radical, about 85 percent of the oxygen is in the cyclopentene products and 15 percent in the initiator fragments in run 11, compared with about 50 percent for each in Run 143. Significant amounts of residue are formed and the yield of epoxide increases as the pressure of cyclopentene is raised. Run 13 represents another threefold increase in cyclopentene pressure with a concomitant increase in rate. The residue and epoxide are now the major products along with substantial amounts of cyclopentadiene and unknown product. In Expts. 11 and 13 the yields of CO exceed the yields of methyl radicals produced from the initiator (equivalent to the yield of acetone). Thus cyclopentene is being degraded in part to CO, presumably via decarbonylation of glutaraldehyde. This route requires that some cyclopentene molecules react with several oxygen molecules, giving bifunctional products which may escape detection except possibly as residue. There is a rough relationship between yields of excess CO and yields of residue in these experiments.

A further comparison of Runs 11 and 13 reveals a drop in hydroperoxide yield despite increases in cyclopentene pressure and oxygen consumption. While this change might be associated with the reaction of hydroperoxide with cyclopentene to give epoxide, o evidence was found for this reaction in one experiment at a lower pressure (Section 5.3).

5.2. Oxidation of Cyclopentene at 100°

Several experiments were made at 100° at high pressures in hopes of obtaining a simpler product mixture and of observing the effect of temperature. Run 15 in Table V was intended to be carried out in the gas phase at 100°. It is a little faster than expected from the 155° experiment and known activation energies and so a little reaction may have occurred in the liquid phase during the initial warm-up period.

Examination of the products of this gas-phase Expt. 15 at 100° showed the presence of substantial amounts of residue and epoxide and an excess of CO over the number of methyl radicals produced, as in experiments at 155°. Possibly as much as a third of the oxygen was present

Table V

OXIDATION OF CYCLOPENTENE AT 100° AND 155°

| Run Number	143	11	13	15	17
Temperature	155°	155°	155°	100°	100°
Time (min)	40	40	45	900	20
Reaction Volume (ml)	500	105	100	107	1.18 liquid
Reactants	micromols				
$t\text{-}Bu_2O_2$	139	40	48	21	2.1
O_2	995	1100	1156	2362	822
C_5H_8 (Pressure)	3420 (183 mm)	4500 (1140 mm)	12850 (3080 mm)	6000 (1415 mm)	11800
Products	micromols				
$-O_2$	323	350	1125	448	340
$-Bu_2O_2$	87	23	27	-	-
$t\text{-}Bu_2O_2$ Calc.[a]	74	21	28	.61	0.002
CO	49	52	153	14	0
Acetone	159	34	41	-	-
MeOH	39	10	-	-	-
$t\text{-}BuOH$	39	13	13	-	-
C_5H_6	26	22	81	18	Trace
Epoxide	29	45	110	46	19
Cyclopentenone	42	37	84	54	58
Cyclopentenol	19	2	19	8	26
C_5H_7OOH	41	52	29	27	316
Residue	~ 0	50[c] (5 mg)	300[c] (30 mg)	100[c] (10 mg)	~ 0
Unknown	21	10	55	~ 0	9.4
$-O_2 -(BuO\cdot)$	2.2	8.1	21	370	> 10,000

[a] Cf. note b to Table I.

[b] Total titrated hydroperoxides, mostly or entirely $C_5H_7O_2H$; 75% of latter would appear after g.l.c. and in Table above as 5/7 cyclopentenone and 2/7 cyclopentenol.

[c] Calculated as $(C_5H_8O_2)_n$.

as products of an apparent addition mechanism. A liquid-phase run (No. 17) was made for comparison with the gas-phase runs and with earlier work by Van Sickle in the liquid phase at 50°. Almost 93 percent of the oxygen appeared as hydroperoxide but small amounts of epoxide and unknown product are present. Only a trace of cyclopentadiene was found. Thus the course of the liquid-phase reaction was substantially unchanged between 50° and 100° and the course of the vapor-phase reaction is much the same at 100° as at 155°.

We offer the following tentative explanation of the difference between the liquid-phase and vapor-phase oxidations of cyclopentene. Products of the addition of peroxy radicals to cyclopentene (cyclopentene oxide, CO from its oxidation, and maybe some polymer) may appear more important in the vapor phase because an essential step in the hydrogen transfer chain
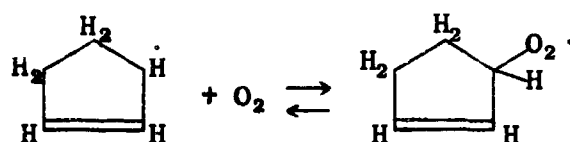
becomes reversible at decreased pressures and increased temperatures. The large proportions of residue may represent secondary condensation or polymerization reactions of primary products such as cyclopentenone, cyclopentadiene, and cyclopentene oxide, possibly in liquid films on the vessel walls.

5.3. Thermal Vapor-Phase Decompositions of Cyclopentene Hydroperoxide

One experiment at 155° will be discussed first; then several at 100°. A mixture of 211 μmols of cyclopentenyl hydroperoxide and 2700 μmols (149 mm) of cyclopentene was heated without oxygen for 30 minutes at 155°. Titration of the mixture indicated that 105 μmols of hydroperoxide (50 percent) had decomposed. Gas chromatographic analysis of a nitrobenzene solution showed only a trace of cyclopentene oxide and about 30 percent of the original hydroperoxide in the form of ketone and alcohol (5:2). A blank experiment without heating and with nitrobenzene gave a 98 percent recovery of hydroperoxide (titrimetric) and about 75 percent recovery (in the form of ketone and alcohol) when pyrolyzed in the gas chromatograph. Except for the absence of oxygen and initiator, the 155° conditions are close to those in Oxidation Expt. 143 where epoxide was formed. We conclude that the gas-phase decomposition of cyclopentenyl hydroperoxide at 155° does not proceed through peroxy radicals and does not react otherwise with cyclopentene to give epoxide.

Gas chromatographic analysis for hydroperoxide by pyrolysis to ketone and alcohol gives variable results depending on whether the peroxide is pyrolyzed in the presence of cyclopentene. In the presence of an excess of olefin, only 25 percent of the peroxide is accounted for (see Table V, Expt. 17). These results resemble those with tetralin hydroperoxide and support the idea that alkoxy and alkylperoxy radicals may add to cyclopentene under some conditions.

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Section 4.3 showed that cyclopentene is an effective retarder for the alkoxy-radical-induced decomposition of t-butyl hydroperoxide in the gas phase at 100°. One might therefore expect vapor-phase oxidations of moderate concentrations of cyclopentene to produce good yields of hydroperoxide. However, Table V shows that such oxidations in fact produce low yields of hydroperoxide in comparison with liquid-phase experiments. In order to explain this result, we have studied the thermal gas-phase decomposition of cyclopentenyl hydroperoxide at 100° in the presence of about three atmospheres of cyclopentene. Mixtures of about 1 mol % hydroperoxide in cyclopentene (with and without $t-Bu_2O_2$) were degassed and sealed off in Pyrex bulbs, heated for several hours at 100°, and then analyzed for hydroperoxide and other products (after reducing the hydroperoxide with triphenylphosphine).

Results are summarized in Table VI. In Expts. 1 and 2, the decomposition of cyclopentenyl hydroperoxide without initiator was 8-10 times as fast as the decomposition of t-butyl hydroperoxide with added initiator (Expt. 43D in Table II). Added benzene (Expt. 3) cut the rate of decomposition in half. When aged cyclopentene containing about 1% oxidation products (mostly hydroperoxide) was used in place of the purified cyclopentene, or when the initial hydroperoxide concentration was doubled (Expt. 8), the rate increased 4- to 6-fold; added $t-Bu_2O_2$ was without effect (Expts. 4 and 5). The near-equivalence of the effects of no solvent (Expt. 7), cyclopentene, and cyclopentane, the mild retarding effect of benzene, and the absence of catalysis by $t-Bu_2O_2$ seem to exclude a radical chain mechanism. Further, the low yields of epoxide, both at 100° and 155°, exclude much action of the solvent with peroxy radicals:

$$C_5H_7O_2 \cdot + C_5H_8 \longrightarrow C_5H_7O \cdot + C_5H_8O$$

The retarding effect of benzene in Expt. 3 resembles the larger effect of this solvent in the liquid-phase decomposition of cyclopentenyl hydroperoxide in other work by Dr. D. E. Van Sickle in this laboratory. In that work kinetic studies indicated that a hydroperoxide dimer is the less stable form, a conclusion that can be extended to the present work in view of the approximate second-order rate dependence on hydroperoxide. Possibly benzene complexes with monomeric hydroperoxide and thus reduces the concentration of the less stable dimer. Monomeric peroxide should be stable up to $175-200^\circ$ toward homogeneous non-chain decomposition.[7]

Experiment 6 with oxygen, in Table VI, gave a large amount of insoluble yellow residue together with substantial amounts of epoxide, in contrast to the non-oxidative runs. We estimate from Run 15 in Table V that almost all of the oxygen originally present was consumed during reaction. Thus the volatile products account for about one-third of the O_2 put in (after allowing for the oxygen in the hydroperoxide decomposed) and the remainder must be mostly in the residue. These analytical results parallel results in oxidations at 100° and 150° (Sections 5.1 and 5.2).

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[7] S. W. Benson, J. Chem. Phys., 40, 1007 (1964).

An experiment similar to No. 6 was made to prepare and characterize the residue. About half the cyclopentene-insoluble residue was found to dissolve in benzene and the remainder in ethanol. The benzene fraction contained up to 50% ketone and alcohol together with small amounts of other volatile unidentified products. Elemental analyses indicate an average composition of $C_5H_{7.4}O_{1.3}$ and molecular weight of 110. Ethanol-soluble

Table VI

THERMAL DECOMPOSITION OF CYCLOPENTENYL HYDROPEROXIDE IN THE GAS PHASE AT 100°

Run Number	1	2	3	4	5	6	7	8
Reaction Time (Min)	470	470	461	480	480	900	485	420
Reactants - mmols/liter								
C_5H_7OOH[a]	1.07	1.13	1.05	1.85	2.03	1.80	1.04	2.15
C_5H_8[b]	123-p	0	0	131-i	125-i	127-i	0	0
$t-Bu_2O_2$	0	0	0	1.05	0	1.02	0	0
Other		101 C_5H_{10}	119 C_6H_6			10.2 O_2		
Products - mmols/liter								
Final RO_2H	0.73	0.83	0.92	0.27	0.09	0.11	0.61	0.45
$-\Delta RO_2H$	0.34	.30	0.13	1.58	1.94	--	0.43	1.70
Cyclopentene Oxide	0.04	0	--	0	0.13	1.84	0	0
Cyclopentenol[c]	0.20	0.10	.04	0.56	0.97	0.94	0.40	0.43
Cyclopentenone[d]	0.17	0.17	.11	0.40	0.69	2.74	0.22	0.83
Other						50-60 mg residue		
Σ Products	1.14	1.10	1.07	1.23	1.87	5.63	1.23	1.71
Average Rates - mols/liter min x 10^7								
$-d[RO_2H]/dt$	7.2	6.5	3.2	33	40.5	--	8.9	40.5
$k_2 = \text{Rate}/[ROOH]_0^2$	6.3	5.1	1.3	9.6	9.8		8.2	8.8

[a] C_5H_7OOH 87% pure; contained 8% 3-cyclopentenone; includes C_5H_7OOH present in impure C_5H_8 where applicable (see b).
[b] Designated "p" or "i" to indicate whether C_5H_8 contained 0 or 1% of hydroperoxide impurities.
[c] Corrected for ROOH converted to alcohol by $(C_6H_5)_3P$.
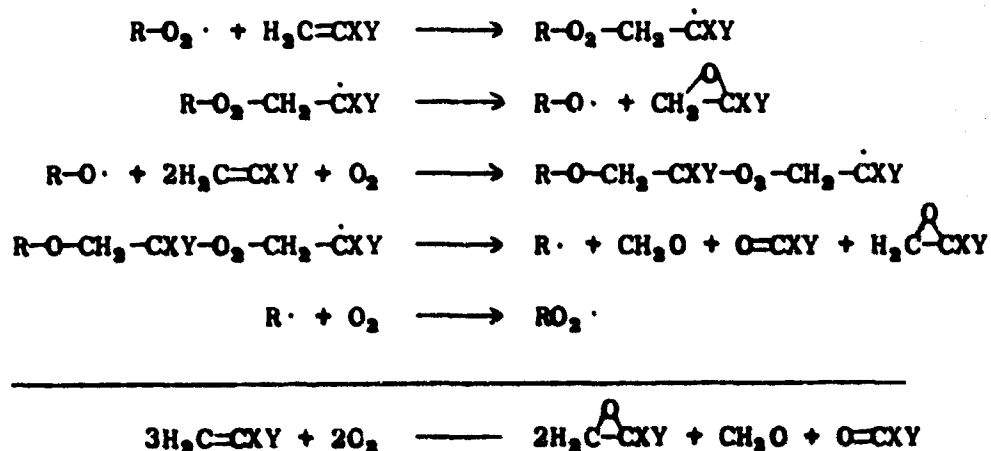[d] Corrected for ketone present in C_5H_7OOH.

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material gave no peaks on the gas chromatograph. Elemental analyses indicate an average composition of $C_5H_{8.1}O_{2.4}$, indicating the presence of peroxide links and/or glycol units. The average molecular weight found, 149, belies its obvious involatility.

6. GAS-PHASE OXIDATION OF ISOBUTYLENE

Unpublished work in this Laboratory led to the conclusion that in the gas-phase oxidation of isobutane at 155° most of the hydrocarbon is attacked by alkoxy rather than by alkylperoxy radicals. At higher temperatures, rearrangements of peroxy radicals become important but chain propagation still depends mostly on hydroxy or alkoxy radicals. The purpose of this section is to extend these ideas (without any new experimental work) to the oxidation of isobutylene and, by implication, to other alkenes which react mostly by the addition mechanism.

In liquid-phase oxidations of α-methylstyrene[8] and di-isobutylene[9] under conditions where every β-peroxyalkyl radical rearranges to epoxide and alkoxy radical, the following idealized scheme is approached:[8]

$$R-O_2 \cdot + H_2C{=}CXY \longrightarrow R-O_2-CH_2-\overset{\cdot}{C}XY$$

$$R-O_2-CH_2-\overset{\cdot}{C}XY \longrightarrow R-O \cdot + CH_2\overset{O}{\overset{\triangle}{}}CXY$$

$$R-O \cdot + 2H_2C{=}CXY + O_2 \longrightarrow R-O-CH_2-CXY-O_2-CH_2-\overset{\cdot}{C}XY$$

$$R-O-CH_2-CXY-O_2-CH_2-\overset{\cdot}{C}XY \longrightarrow R \cdot + CH_2O + O{=}CXY + H_2\overset{O}{\overset{\parallel}{C}}CXY$$

$$R \cdot + O_2 \longrightarrow RO_2 \cdot$$

$$3H_2C{=}CXY + 2O_2 \longrightarrow 2H_2\overset{O}{\overset{\parallel}{C}}CXY + CH_2O + O{=}CXY$$

This scheme was developed to account for the products of liquid-phase oxidations with long kinetic chains. It will now be used to account for the products of gas-phase oxidation of isobutylene, with the following postulates: 1. Formation of epoxide measures additions of peroxy radicals to double bonds. 2. Formation of acetone (and formaldehyde) measures additions of alkoxy or hydroxy radicals to double bonds.

In Table VII these postulates are applied to the results of Skirrow and Williams[10] and to our own results at 147° and 197° with isobutylene. The table indicates that alkoxy radicals are more important than peroxy radicals in chain propagation under all conditions listed in Table VII. The first three experiments suffer from either poor material balances (partly due to formation of polymer) or high conversion; they suggest that alkoxy radicals become more important at higher temperatures, possibly due to rearrangement of peroxy to alkoxy (or hydroxy) radicals.

[8] F. R. Mayo and A. A. Miller, J. Am. Chem. Soc., 80, 2480 (1958).

[9] F. R. Mayo, ibid., 2497.

[10] G. Skirrow and A. Williams, Proc. Royal Soc., A268, 537 (1962).

Table VII

INITIAL PRODUCTS OF GAS-PHASE OXIDATION OF ISOBUTYLENE

	Fraction of $i\text{-}C_4H_8$ Reacting Found as		
	Acetone (Addn. of RO·)	Epoxide (Addn. of RO_2·)	Methacrolein (Abstraction of H·)
$t\text{-}Bu_2O_2$ initiation at 147°[a]	31%	27%	8%
$t\text{-}Bu_2O_2$ initiation at 197°[a]	33%	18%	0
Uninitiated at 252°[b]	37%	22%	7%
Uninitiated at 320°[c]	66%	20%	14%

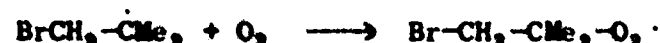[a] Unpublished work by Dr. P. S. Fredricks.
[b] Ref. 10, at 88% conversion of $i\text{-}C_4H_8$.
[c] Ref. 10, estimated for 23% conversion of $i\text{-}C_4H_8$.

The low extents of reaction (about 1.5 molecules of isobutylene per $t\text{-}Bu_2O_2$ decomposed at 147°, about 1.2 molecules of isobutylene per $t\text{-}Bu_2N_2$ decomposed at 197°) are due partly to the low reactivity of peroxy radicals toward the hydrocarbon, partly to the reversibility of the addition of peroxy radicals to double bonds, but mostly due to the ready availability of chain-terminating reactions and the low concentrations of isobutylene in the gas phase.

Some other aspects of the work of Skirrow and co-workers will now be considered. Hurst, Skirrow, and Tipper[11] studied the hydrogen bromide-catalyzed oxidation of isobutylene at 145° and 195° and Skirrow and Williams[10] studied the uncatalyzed oxidation at 252° and 320°. With hydrogen bromide in a boric acid-coated vessel at 145°, the primary product, in good yield, is $Br\text{-}CH_2\text{-}CMe_2\text{-}O_2H$. This product establishes that hydrogen bromide catalysis involves the reactions

$$BrCH_2\text{-}CMe_2\text{-}O_2\cdot \; + \; HBr \longrightarrow R\text{-}O_2H \; + \; Br\cdot$$

$$Br\cdot \; + \; H_2C{=}CMe_2 \longrightarrow BrCH_2\text{-}\dot{C}Me_2$$

$$BrCH_2\text{-}\dot{C}Me_2 \; + \; O_2 \longrightarrow Br\text{-}CH_2\text{-}CMe_2\text{-}O_2\cdot$$

These reactions are analogous to those proposed for the hydrogen bromide-catalyzed oxidation of isobutane.[12] That oxidation stopped when the hydrogen bromide was exhausted supports our conclusion that addition of peroxy radicals to isobutylene is relatively difficult. At 195°, hydrogen abstraction begins to compete with the last reaction above:

[11] P. Hurst, G. Skirrow and C. F. H. Tipper, ibid., 405
[12] F. F. Rust and W. E. Vaughan, Ind. Eng. Chem. 41, 2595 (1949).

$$Br \cdot + H_2C{=}CMe_2 \longrightarrow H_2C{=}CMe{-}CH_2 \cdot + HBr$$
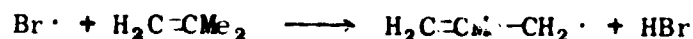
Methallyl hydroperoxide is formed and found as methacrolein, and secondary reactions become generally more important.

The uncatalyzed oxidation[10] requires a temperature of 250°. Here and at 320°, the principal and earliest detectable products are nearly equal quantities of acetone and formaldehyde. The next most important product is isobutyraldehyde, from rearrangement of isobutylene oxide. Less methacrolein is found. Skirrow and Williams propose that the carbonyl compounds arise by the sequence

$$HO \cdot + H_2C{=}CMe_2 \longrightarrow HO{-}CH_2{-}\overset{\cdot}{C}Me_2$$

$$HO{-}CH_2{-}\overset{\cdot}{C}Me_2 + O_2 \longrightarrow HO{-}CH_2{-}CMe_2{-}O_2 \cdot$$

$$HO{-}CH_2{-}CMe_2{-}O_2 \longrightarrow HO \cdot + CH_2O + CH_3COCH_3$$
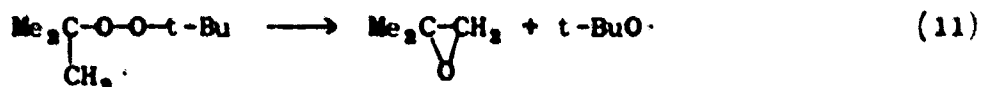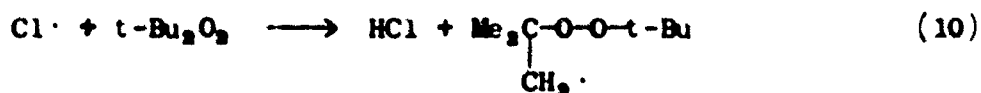
without specifying details of the rearrangement. This proposal is consistent with other high-temperature rearrangements of peroxy radicals and with our proposal that acetone measures additions of hydroxy and alkoxy radicals.

Thus our postulates seem to be useful in correlating oxidations of unsaturated compounds which oxidize by the addition mechanism.

7. HYDROGEN-CHLORIDE CATALYZED OXIDATIONS
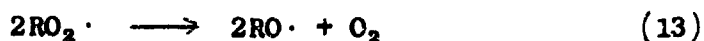
7.1. Theoretical Background

Hydrogen chloride is known to catalyze the pyrolysis of di-t-butyl peroxide.[13] Recently Flowers, Batt, and Benson[14] have established the over-all rate law for the reaction and have confirmed that the catalytic effect of HCl on di-t-butyl peroxide (25 times uncatalyzed rate at $90{-}120^O$) is due to intervention of two fast chain-transfer steps.

$$t{-}BuO \cdot \text{ (or } Me \cdot) + HCl \longrightarrow t{-}BuOH \text{ (or } MeH) + Cl \cdot \qquad (9)$$

$$Cl \cdot + t{-}Bu_2O_2 \longrightarrow HCl + \underset{\underset{CH_2 \cdot}{|}}{Me_2C{-}O{-}O{-}t{-}Bu} \qquad (10)$$

$$\underset{\underset{CH_2 \cdot}{|}}{Me_2C{-}O{-}O{-}t{-}Bu} \longrightarrow Me_2\underset{O}{\overset{}{C{-}CH_2}} + t{-}BuO \cdot \qquad (11)$$

These results suggested that a similar catalytic scheme might apply in low-temperature oxidations of hydrocarbons which involve alkoxy radicals in short-chain or non-chain reactions.

[13] J. H. Raley, F. F. Rust, and W. E. Vaughan, J. Am. Chem. Soc. **70**, 2767 (1948).

[14] M. Flowers, L. Batt, and S. W. Benson, J. Chem. Phys., **37**, 2662 (1962).

$$R \cdot + O_2 \longrightarrow RO_2 \cdot \qquad (12)$$

$$2RO_2 \cdot \longrightarrow 2RO \cdot + O_2 \qquad (13)$$

$$2RO_2 \cdot \longrightarrow \text{termination} \qquad (14)$$

$$RO \cdot + HCl \longrightarrow ROH + Cl \cdot \qquad (15)$$

$$Cl \cdot + RH \longrightarrow HCl + R \cdot \qquad (16)$$

$$2RO \cdot \longrightarrow \text{termination} \qquad (17)$$

Chain steps 15 and 16 here are identical in kind with steps 9 and 10 in the peroxide decomposition. They replace the slower step

$$RO \cdot + RH \longrightarrow ROH + R \cdot \qquad (18)$$

and correspond to the catalytic effect of hydrogen bromide in reactions of peroxy radicals with hydrocarbons (Section 6). For significant catalysis, reactions 15 and 16 must be faster than 17 and 18, and chains must be carried mostly by alkoxy rather than by peroxy radicals. The last restriction is the most important one for it requires that most of the interactions of peroxy radicals must be nonterminating (reaction 13) rather than terminating (reaction 14). With $t\text{-BuO}_2 \cdot$ radicals, k_{13}/k_{14} is about 7 in solution[15] and so the maximum conversion of isobutane to t-butanol under these conditions would be 14 molecules per initiating radical pair (the conversion might be much less than 1.0 without catalysis at low temperatures). Data are meagre, but present indications are that a favorable ratio of k_{13}/k_{14} is possible only with tertiary peroxy radicals and that the ratio is less than one, probably nearer zero, with primary and secondary peroxy radicals.

We have tried to get conclusive evidence of catalysis by hydrogen chloride of a free radical chain oxidation reaction by the three different methods indicated in Sections 7.2 to 7.4. We have indications of an interesting effect, but not the clear proof that we seek.

7.2. Vapor-Phase Photo-Oxidation of Isobutane with Hydrogen Chloride

Three experiments have been made with 1500 μmols of isobutane, 200 μmols of oxygen, and 150 μmols of HCl to test the idea above. The mixtures were irradiated in 100 ml quartz vessels with mercury lamps (Penray SC-1 and Westinghouse H85A3) or sunlight, HCl serving as the photoinitiator. In each case a different and rather complex mixture of products was found. Six-hour irradiation with the H85A3 lamp gave 17 μmols of t-butyl chloride and about 10-15 μmols of other products. There was no dark reaction and a blank without HCl gave no evidence of reaction. t-Butanol, methanol, t-butyl chloride, i-butyl chloride, acetaldehyde, and acetone were identified with some certainty by g.l.c. retention times.

[15]R. Hiatt, J. Clipsham, and T. Visser, "Induced Decomposition of t-Butyl Hydroperoxide," to be submitted to Can. J. Chem.

The chlorinated products apparently arose from secondary reactions of the alcohols with HCl, since HCl reacted at a substantial rate with t-BuOH even in the vapor phase at 25°. The differences in product composition from run to run probably arise from secondary photochemical reactions which differ with the u.v. source in each experiment.

Considerable difficulty was encountered in measuring noncondensables due to fouling of the Cu-CuO furnace by HCl which escaped retention in two liquid nitrogen traps. The necessarily crude results indicate both oxygen consumption and CO production. A trap packed with sodium carbonate, p-dimethylaminobenzaldehyde, or auramine[14] has been found to be reasonably effective in removing HCl prior to collection of products in the first cold trap.

It is apparent that HCl can be photodissociated to give atoms capable of abstracting hydrogen from isobutane at 25°, yielding H_2 or HCl. However, the chain length of the oxidation reaction cannot be estimated until the rate of initiation is known. Irradiation of HCl and i-BuH without oxygen in quartz with an H85-A3 lamp for a substantially longer time than used for the oxidation run gave only a trace of t-BuCl and no evidence for hydrogen. An unknown peak of substantial proportion ($\sim$ 20 μmols) appeared in the chromatogram at a retention time suggestive of a C_3 hydrocarbon. However, the same material is produced by irradiation of HCl alone in quartz and its identity (not $SiCl_4$) remains a mystery. The absence of organic products in this reaction indicates, but does not establish, long chains in the oxidation.

7.3. Vapor-Phase Photo-Oxidation of Isobutane

Our next effort to establish hydrogen chloride catalysis used t-butyl hypochlorite as photoinitiator for isobutane oxidations. Reactions of chlorine atoms with isobutane provide HCl in situ and the consumption of hypochlorite can be measured iodometrically.

Two experiments in 100 ml glass bulbs at 25-30° with 0.2 and 0.7 atmospheres of isobutane (7.1 mM and 29mM), oxygen (2.5 mM), and 100 μmols t-BuOCl (1 mM) gave nearly the same average rates of oxidation, 1.75×10^{-6} mol/liter min over 16 hours. A similar experiment with oxygen and hypochlorite but without isobutane consumed oxygen at the rate of 1.26×10^{-6} mol/liter min in 15 hours. No hypochlorite remained in any of these experiments, indicating chain lengths were of the order of 0.5; possibly these reactions had stopped some time before the measurements were made. Analysis of one isobutane run showed the presence of CO, acetone, t-BuOH, and both t- and isobutyl chlorides, but only 30% of the oxygen consumed (176 μmols) was accounted for. The blank run gave few volatile products; most of the material ($\sim$ 10 mg) was an unidentified, colorless, nonvolatile oil.

The rate of oxidation of isobutane at 30° may be calculated from the value of $k_p/k_t^{1/2}$ in Section 4.4 and the known average values of R_i (two radicals per t-BuOCl and [iBuH] and inserting these into the simple rate expression

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$$R_{O_2} = (k_p/k_t^{1/2})\, R_i^{1/2}[RH] = (\frac{0.010}{60} \times \frac{0.001}{960})^{1/2} \times 0.0029 =$$

$$5 \times 10^{-10} \text{ mol/liter min}$$

Thus the observed rate of oxidation (of both t-BuOCl and i-BuH) is ~ 5000 times as fast as would be expected had the reaction mechanism remained the same as at 80-100°. If the oxidation was complete in less than the measured time, the average rate of oxidation at 25° would be proportionately greater, giving a still larger difference between calculated and observed rates.
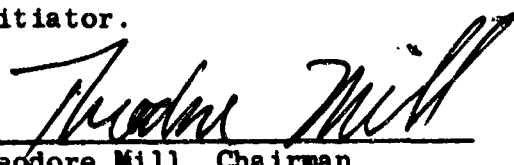
7.4. Liquid-Phase Photo-Oxidation of Decalin with Hydrogen Chloride
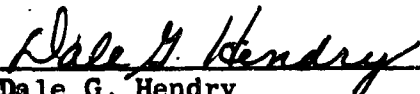
An effort to establish hydrogen chloride catalysis in the liquid-phase oxidation of decalin showed only a small catalytic effect. However, the control experiment gave mostly hydroperoxide. Since most of the chains were carried by peroxy rather than alkoxy radicals, this test is also unsatisfactory.

Our experiments employed 20 mol % solutions of decalin (cis-trans mixture) in o-dichlorobenzene and 0.0542 M ABN. Rates were followed manometrically over about one half-life of the initiator at 50°. A solution without HCl took up 67 mmols/liter of oxygen in 95 hours, of which 79% could be titrated as hydroperoxide. A similar solution with 0.064 M HCl took up 107 mmols/liter of oxygen of which only 8% appeared as hydroperoxide. Treatment of the uncatalyzed oxidation mixture with HCl at 50° destroyed the hydroperoxide, probably the primary product in both experiments.
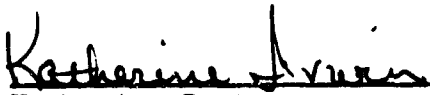
7.5. Proposed Work on HCl Catalysis

The apparent marked catalysis by HCl in the oxidation of isobutane at 30° (using t-butyl hypochlorite) will be checked by additional experiments with chlorine or hypochlorite initiator. Some low-pressure oxidations of isobutane at 100° will be made using HCl and di-t-butyl peroxide initiator.

Theodore Mill, Chairman
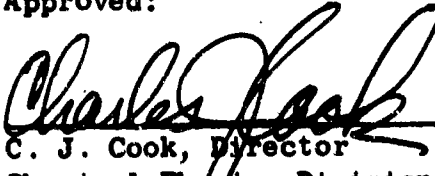Department of Physical-Organic
Chemistry

Dale G. Hendry
Senior Organic Chemist

Jane Castleman
Organic Chemist

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